PHYSICAL REVIEW A VOLUME 38, NUMBER 3 AUGUST 1, 1988

Density-functional theory of many-electron systems subjected to time-dependent electric and magnetic fields

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(Received 22 September 1987)

A time-dependent density-functional formalism is developed for many-electron systems subjected to external electric and magnetic fields with arbitrary time dependence. The single-particle current density is shown to determine uniquely the time-dependent scalar and vector potentials characterizing the system, and hence also the many-particle wave function. A Levy-type universal functional is defined, and practical schemes for the calculation of electron density and the current density through hydrodynamical as well as a set of single-particle Kohn-Sham-like equations are proposed. The gauge invariance of the present self-consistent formalism is also proved.

I. INTRODUCTION

Density-functional theory[1,2] (DFT) for stationary properties of many-electron systems is well established as a conceptually simple and practically useful tool in various branches of physics and chemistry.[3,4] This theory was formally born with the pioneering work of Hohenberg and Kohn,[1] which proves that the external potential $v(\mathbf{r})$ characterizing a many-electron system is a unique functional (apart from an arbitrary additive constant) of its single-particle density $\rho(\mathbf{r})$. The proof, which was originally given for a nondegenerate ground state,[1] has subsequently been extended to include the degenerate case,[5] some excited states,[6] small time-dependent (TD) perturbations,[7] and systems characterized by oscillating TD potentials.[8] An extension to the case of the arbitrary TD situation has been provided only recently by Runge and Gross (RG),[9] who proved that the mapping between the TD density $\rho(\mathbf{r},t)$ and the TD potential $v(\mathbf{r},t)$ is unique. The scope of this work has been further broadened through the construction[10] of a Levy-type functional[11] for the TD case and also extensions to TD ensembles[12] as well as multicomponent systems.[13] The elegant proof of RG (Ref. 9) has, however, faced criticisms[14,15] and has, therefore, been reexamined by Dhara and Ghosh,[16] who replied to the criticisms raised by Xu and Rajagopal[14] but simultaneously pointed out the limitations of the RG work—thus presenting a more transparent view of the actual status of time-dependent density-functional theory (TDDFT). They have also demonstrated[16] an explicit construction of $v(\mathbf{r},t)$ from either $\rho(\mathbf{r},t)$ or the current density $\mathbf{j}(\mathbf{r},t)$ through the equations of quantum hydrodynamics[17] for a single-particle system. This unique density-to-potential mapping is possible for both bound and scattering states of the unperturbed stationary system.[16]

The TDDFT available[7-10,12-16] so far has, however, been restricted to scalar potentials alone and thus excludes situations involving vector potentials, e.g., when a TD magnetic field is applied. Thus it does not cover a very important class of TD problems, viz., the interaction of electromagnetic radiation with matter. The objective of the present work is to develop a TDDFT for systems characterized by the scalar as well as vector potentials with arbitrary time dependence.

In what follows, we first establish in Sec. II a Hohenberg-Kohn-like theorem demonstrating the uniqueness of the density-to-potential mapping. Besides showing the stationary property of the action-integral-like energy density functionals, a Levy-type construction is also proposed for the same. The hydrodynamic equations describing the time evolution of the density and the current density are discussed. A practical scheme analogous to the Kohn-Sham[2] procedure is then developed for the direct calculation of the charge density and the current density. Finally, we offer a few concluding remarks in Sec. III.

II. FORMALISM

The system that we consider consists of N electrons moving under the influence of their mutual Coulombic interaction along with the single-particle external potential due to the nuclei $v(\mathbf{r})$, an additional TD scalar potential $\phi(\mathbf{r},t)$, and the TD vector potential $\mathbf{A}(\mathbf{r},t)$. The corresponding many-electron wave function $\psi(\mathbf{r}_1,\mathbf{r}_2,\ldots,\mathbf{r}_N,t)$ satisfies the TD Schrödinger equation

$$[i\hbar(\partial/\partial t)-\hat{H}]\psi=0 , \tag{1}$$

and the Hamiltonian $\hat{H}$ is given by

$$\hat{H}=(1/2m)\sum_k[\hat{\mathbf{p}}(\mathbf{r}_k)+(e/c)\mathbf{A}(\mathbf{r}_k,t)]^2+V-e\sum_k\phi(\mathbf{r}_k,t)+U , \tag{2}$$

where $V(\equiv e\sum_k v(\mathbf{r}_k))$ and $U(\equiv\sum_{k<l}(e^2/|\mathbf{r}_k-r_l|))$ denote the one-electron and two-electron potential opera-

tors, respectively. Here, we consider the charge of the electron to be $-e$ and its mass to be m. The expression for $\hat{H}$ can be rewritten as

$$\hat{H} = -(\hbar^2/2m)\sum_k \nabla_k^2 - i(e\hbar/mc)\sum_k \mathbf{A}_k\cdot\nabla_k + (e^2/2mc^2)\sum_k \mathbf{A}_k^2 + V - e\sum_k \phi_k + U \ , \tag{3}$$

by using the Coulomb gauge $\nabla\cdot\mathbf{A}=0$ and the notations $\phi_k \equiv \phi(\mathbf{r}_k,t)$ and $\mathbf{A}_k \equiv \mathbf{A}(\mathbf{r}_k,t)$. For simplicity, here, the spin-dependent terms have been omitted; an extension to spin-density-functional theory is, however, straightforward.

The single-particle density $\rho(\mathbf{r},t)$ and the current density $\mathbf{j}(\mathbf{r},t)$ are obtained from the relations

$$\rho(\mathbf{r},t) = \langle\psi|\hat{\rho}|\psi\rangle \ , \tag{4a}$$

$$\mathbf{j}(\mathbf{r},t) = \langle\psi|\hat{\mathbf{j}}|\psi\rangle \ , \tag{4b}$$

where the density and the current-density operators $\hat{\rho}$ and $\hat{\mathbf{j}}$ are, respectively, given by

$$\hat{\rho} = \sum_k \delta(\mathbf{r}-\mathbf{r}_k) \tag{5a}$$

and

$$\begin{aligned}\hat{\mathbf{j}} &= (1/2m)\sum_k [\hat{\mathbf{p}}_k\delta(\mathbf{r}-\mathbf{r}_k)+\delta(\mathbf{r}-\mathbf{r}_k)\hat{\mathbf{p}}_k] \\ &= -(i\hbar/2m)\sum_k [\nabla_k\delta(\mathbf{r}-\mathbf{r}_k)+\delta(\mathbf{r}-\mathbf{r}_k)\nabla_k] \\ &\quad + (e/mc)\sum_k \mathbf{A}_k\delta(\mathbf{r}-\mathbf{r}_k) \ ,\end{aligned} \tag{5b}$$

where $\hat{\mathbf{p}}_k$ is the canonical momentum operator. The formal theory that now follows aims at describing the system with these density quantities as basic variables.

A. Existence and uniqueness of the density functionals

The following two theorems prove the uniqueness of the density-to-potential mapping and the stationarity properties of density functionals.

Theorem 1. In a many-electron system characterized by any single-particle time-dependent scalar potential $\phi(\mathbf{r},t)$ and vector potential $\mathbf{A}(\mathbf{r},t)$ which can be expanded into Taylor series with respect to the time coordinate around $t=t_0$, the current density $\mathbf{j}(\mathbf{r},t)$ of the system determines both the potentials uniquely.

Proof. Let $\phi(\mathbf{r},t)$ and $\phi'(\mathbf{r},t)$ be two scalar potentials differing by more than a merely TD function and $\mathbf{A}(\mathbf{r},t)$ and $\mathbf{A}'(\mathbf{r},t)$ be two different vector potentials, i.e., $\phi(\mathbf{r},t)-\phi'(\mathbf{r},t)\neq C(t)$ and $\mathbf{A}(\mathbf{r},t)-\mathbf{A}'(\mathbf{r},t)\neq 0$. Since the potentials can be expanded into Taylor series around $t=t_0$, there must exist at least one time derivative of the potentials which differ by more than a constant (considered as zero for convenience). Let the minimal nonnegative integer which must exist be k for the scalar potential and l for the vector potential, i.e.,

$$(\partial^n/\partial t^n)[\phi(\mathbf{r},t)-\phi'(\mathbf{r},t)]\,|_{t=t_0} \begin{cases}\neq 0, & n=k \\ =0, & 0\le n<k\end{cases} \tag{6a}$$

and

$$(\partial^n/\partial t^n)[\mathbf{A}(\mathbf{r},t)-\mathbf{A}'(\mathbf{r},t)]\,|_{t=t_0} \begin{cases}\neq 0, & n=l \\ =0, & 0\le n<l \ .\end{cases} \tag{6b}$$

Here, without any loss of generality we consider only the states evolving from a fixed initial state and therefore at the initial time $t=t_0$, the wave functions as well as the densities corresponding to the two sets of potentials $\{\phi,\mathbf{A}\}$ and $\{\phi',\mathbf{A}'\}$ are assumed to be identical, i.e., $\psi(t_0)=\psi'(t_0)=\psi^0$; $\rho(t_0)=\rho'(t_0)$; $\mathbf{j}(t_0)=\mathbf{j}'(t_0)$; and the potentials themselves are also identical, viz., $\phi(t_0)=\phi'(t_0)$; $\mathbf{A}(t_0)=\mathbf{A}'(t_0)$.

We now proceed to prove that if either (6a) or (6b) is satisfied, the current densities $\mathbf{j}(\mathbf{r},t)$ and $\mathbf{j}'(\mathbf{r},t)$, which were identical at $t=t_0$, would differ infinitesimally later than t_0, by showing that there exists some minimal integer k' such that

$$(\partial^{k'}/\partial t^{k'})[\mathbf{j}(\mathbf{r},t)-\mathbf{j}'(\mathbf{r},t)]\,|_{t=t_0}\neq 0 \ . \tag{7}$$

Using the equation of motion for an arbitrary TD operator $\hat{\Omega}(t)$,

$$\begin{aligned} i\hbar(d/dt)\langle\psi(t)|\hat{\Omega}(t)|\psi(t)\rangle \\ = \langle\psi(t)|\,i\hbar(\partial/\partial t)\hat{\Omega}(t)+[\hat{\Omega}(t),\hat{H}(t)]\,|\psi(t)\rangle \ ,\end{aligned} \tag{8}$$

one obtains the equation for the time evolution of the current density, viz.,

$$\begin{aligned} i\hbar(\partial/\partial t)\mathbf{j}(\mathbf{r},t) \\ = \langle\psi(t)|\,i\hbar(\partial/\partial t)\hat{\mathbf{j}}(t)+[\hat{\mathbf{j}}(t),\hat{H}(t)]\,|\psi(t)\rangle \ .\end{aligned} \tag{9}$$

Unlike the case with zero magnetic field, the current-density operator of Eq. (5b) explicitly depends on time and also on the vector potential $\mathbf{A}(\mathbf{r},t)$ which is a characteristic of the system. Thus one has

$$(\partial/\partial t)\hat{\mathbf{j}}(t) = (e/mc)\sum_k [(\partial/\partial t)\mathbf{A}_k]\delta(\mathbf{r}-\mathbf{r}_k) \ , \tag{10}$$

and it is easy to show that

$$\begin{aligned} i\hbar(\partial/\partial t)[\mathbf{j}(\mathbf{r},t)-\mathbf{j}'(\mathbf{r},t)]\,|_{t=t_0} &= (e/mc)\Big\langle\psi^0\Big|\, i\hbar\sum_k \delta(\mathbf{r}-\mathbf{r}_k)\frac{\partial}{\partial t}(\mathbf{A}_k-\mathbf{A}'_k)\Big|_{t=t_0}\Big|\psi^0\Big\rangle \\ &= i(e\hbar/mc)\rho(\mathbf{r},t_0)(\partial/\partial t)[\mathbf{A}(\mathbf{r},t)-\mathbf{A}'(\mathbf{r},t)]\,|_{t=t_0} \ ,\end{aligned} \tag{11}$$

where use has been made of the initial conditions at $t=t_0$. In general, an expression for the higher-order derivatives can be obtained by applying the equation of motion (8), say, n times. Thus, after some straightforward algebra, one has the result

$$(i\hbar\partial/\partial t)^n[\mathbf{j}(\mathbf{r},t)-\mathbf{j}'(\mathbf{r},t)]\,|_{t=t_0}=(e/mc)\rho(\mathbf{r},t_0)(i\hbar\partial/\partial t)^n[\mathbf{A}(\mathbf{r},t)-\mathbf{A}'(\mathbf{r},t)]\,|_{t=t_0} + i\hbar(e/m)\rho(\mathbf{r},t_0)\nabla\{(i\hbar\partial/\partial t)^{n-1}[\phi(\mathbf{r},t)-\phi'(\mathbf{r},t)]\,|_{t=t_0}\}\ , \tag{12}$$

where all the lower derivatives [0 to $(n-1)$ for $(\mathbf{A}-\mathbf{A}')$ and 0 to $(n-2)$ for $(\phi-\phi')$] of the differences of the potential terms have been assumed to vanish.

Now, there would arise three distinct possibilities depending on the values of k and l in Eqs. (6a) and (6b).

Case I. $l > k+1$. Consider, in this case, Eq. (12) for $n=k+1$ when clearly only the last term contributes, leading to

$$(i\hbar\partial/\partial t)^{k+1}[\mathbf{j}(\mathbf{r},t)-\mathbf{j}'(\mathbf{r},t)]\,|_{t=t_0}=i\hbar(e/m)\rho(\mathbf{r},t_0)\nabla\{(i\hbar\partial/\partial t)^k[\phi(\mathbf{r},t)-\phi'(\mathbf{r},t)]\,|_{t=t_0}\}\neq 0\ . \tag{13}$$

The two current densities $\mathbf{j}(\mathbf{r},t)$ and $\mathbf{j}'(\mathbf{r},t)$ will therefore differ infinitesimally later than t_0. Further, on using the continuity equation

$$(\partial\rho/\partial t)+\nabla\cdot\mathbf{j}(\mathbf{r},t)=0 \tag{14}$$

and Eq. (13), one has the result

$$(i\hbar\partial/\partial t)^{k+2}[\rho(\mathbf{r},t)-\rho'(\mathbf{r},t)]\,|_{t=t_0}=-i\hbar(e/m)\nabla\cdot[\rho(\mathbf{r},t_0)\nabla\{(i\hbar\partial/\partial t)^k[\phi(\mathbf{r},t)-\phi'(\mathbf{r},t)]\,|_{t=t_0}\}]\neq 0\ . \tag{15}$$

The right-hand side (rhs) of Eq. (15) can easily be shown to be nonzero following Runge and Gross,[9] provided $\rho(\mathbf{r},t_0)$ vanishes rapidly at the boundary.[16] Therefore the two densities $\rho(\mathbf{r},t)$ and $\rho'(\mathbf{r},t)$ will not be identical. (Analogous conclusions follow for a case where the vector potentials $\mathbf{A}$ and $\mathbf{A}'$ are not different, or the system is subjected to an electric field alone.)

Case II. $l < k+1$. Consider again Eq. (12) for $n=l$ to obtain

$$(i\hbar\partial/\partial t)^l[\mathbf{j}(\mathbf{r},t)-\mathbf{j}'(\mathbf{r},t)]\,|_{t=t_0}=(e/mc)\rho(\mathbf{r},t_0)(i\hbar\partial/\partial t)^l[\mathbf{A}(\mathbf{r},t)-\mathbf{A}'(\mathbf{r},t)]\,|_{t=t_0}\neq 0\ . \tag{16}$$

Clearly, then $\mathbf{j}(\mathbf{r},t)$ and $\mathbf{j}'(\mathbf{r},t)$ will differ infinitesimally later than t_0. However, in this case, we are not able to prove that the corresponding densities $\rho(\mathbf{r},t)$ and $\rho'(\mathbf{r},t)$ will also differ. (The same conclusions are valid when the scalar potentials ϕ and ϕ' are identical, or the time dependence arises from the vector potential alone.)

Case III. $l=k+1$. Considering Eq. (12) with $n=l=k+1$, one obtains

$$(i\hbar\partial/\partial t)^{k+1}[\mathbf{j}(\mathbf{r},t)-\mathbf{j}'(\mathbf{r},t)]\,|_{t=t_0}=(e/mc)\rho(\mathbf{r},t_0)(i\hbar\partial/\partial t)^{k+1}[\mathbf{A}(\mathbf{r},t)-\mathbf{A}'(\mathbf{r},t)]\,|_{t=t_0} + i\hbar(e/m)\rho(\mathbf{r},t_0)\nabla\{(i\hbar\partial/\partial t)^k[\phi(\mathbf{r},t)-\phi'(\mathbf{r},t)]\,|_{t=t_0}\}\ . \tag{17}$$

Here, each of the two terms on the rhs is nonzero due to Eq. (6). Let us, however, assume that their sum vanishes and the rhs of Eq. (17) is zero, i.e.,

$$(\partial/\partial t)^{k+1}[\mathbf{A}(\mathbf{r},t)-\mathbf{A}'(\mathbf{r},t)]\,|_{t=t_0}+c\nabla\{(\partial/\partial t)^k[\phi(\mathbf{r},t)-\phi'(\mathbf{r},t)]\,|_{t=t_0}\}=0\ , \tag{18}$$

the divergence of which leads to

$$\nabla^2\chi=0,\quad \chi=\{(\partial/\partial t)^k[\phi(\mathbf{r},t)-\phi'(\mathbf{r},t)]\,|_{t=t_0}\} \tag{19}$$

on using the Coulomb gauge ($\nabla\cdot\mathbf{A}=0$). For a given boundary condition on the potential, as has been argued elsewhere,[16] Eq. (19) has only the trivial solution $\chi=0$ thus contradicting Eq. (6a). Therefore the rhs of Eq. (17) cannot be zero and one is led to the conclusion that $\mathbf{j}(\mathbf{r},t)$ and $\mathbf{j}'(\mathbf{r},t)$ will again be different.

The rhs of Eq. (17) is essentially the kth time derivative of the difference of electric fields $\mathbf{E}(\mathbf{r},t)$ and $\mathbf{E}'(\mathbf{r},t)$, where

$$\mathbf{E}(\mathbf{r},t)=-\nabla\phi(\mathbf{r},t)-(1/c)(\partial/\partial t)\mathbf{A}(\mathbf{r},t) \tag{20}$$

and therefore Eq. (17) can also be rewritten as

$$(i\hbar\partial/\partial t)^{k+1}[\mathbf{j}(\mathbf{r},t)-\mathbf{j}'(\mathbf{r},t)]\,|_{t=t_0} = -i(e\hbar/m)\rho(\mathbf{r},t_0)(i\hbar\partial/\partial t)^k[\mathbf{E}(\mathbf{r},t)-\mathbf{E}'(\mathbf{r},t)]|_{t=t_0}\ . \tag{21}$$

The kth derivative of the two electric fields $\mathbf{E}$ and $\mathbf{E}'$ are different in the case where (6a) and (6b) are satisfied for $l=k+1$.

From the foregoing discussions of the three possible cases, it is now clear that two different sets of potentials $(\phi, \mathbf{A})$ and $(\phi', \mathbf{A}')$ cannot lead to identical $\mathbf{j}(\mathbf{r},t)$. Considering now the special cases of Eq. (12) for $\mathbf{A}=\mathbf{A}'$ with $n=k+1$ and for $\phi=\phi'$ with $n=l$ respectively, one also concludes that if either $\phi(\mathbf{r},t)\neq\phi'(\mathbf{r},t)$ or $\mathbf{A}(\mathbf{r},t)\neq\mathbf{A}'(\mathbf{r},t)$, the corresponding current densities must be different, i.e., $\mathbf{j}(\mathbf{r},t)\neq\mathbf{j}'(\mathbf{r},t)$. (Note that if ϕ and ϕ' differ merely by a TD function, the corresponding wave functions will differ only by a TD phase factor and hence the corresponding densities or current densities would be identical.) Identical densities and identical current densities would also result if $\phi(\mathbf{r},t)$, $\phi'(\mathbf{r},t)$ and $\mathbf{A}(\mathbf{r},t)$, $\mathbf{A}'(\mathbf{r},t)$ are related by a gauge transformation [see Eqs. (B1) in Appendix B]. Fixing the gauge, as has been done here, however, precludes this possibility. Therefore a given current density $\mathbf{j}(\mathbf{r},t)$ can result only from a *unique* scalar and vector potentials $\phi(\mathbf{r},t)$ and $\mathbf{A}(\mathbf{r},t)$, respectively, satisfying the prescribed gauge. (Throughout this paper, the Coulomb gauge is implied and the consideration of gauge transformation will be discussed in Appendix B.) Thus $\mathbf{j}(\mathbf{r},t)$ fixes the potentials and hence the Hamiltonian [the number of electrons N is determined by the integral of the density, i.e., $N=\int d\mathbf{r}\,\rho(\mathbf{r},t_0)$]. Thus all the properties of the system are unique functionals of the current density. The fact that $\mathbf{j}(\mathbf{r},t)$ determines the density uniquely is evident from the continuity equation (14) itself which can be directly employed to obtain $\rho(\mathbf{r},t)$ for a given $\mathbf{j}(\mathbf{r},t)$ since $\rho(\mathbf{r},t_0)$ is known. The functionals involving the wave function ψ can therefore be treated as functionals of the current density $\mathbf{j}(\mathbf{r},t)$ or more conveniently of both $\mathbf{j}(\mathbf{r},t)$ and $\rho(\mathbf{r},t)$, but it is not yet known whether they can be determined uniquely from $\rho(\mathbf{r},t)$ alone.

In general, the wave function is complex and two real quantities, viz., the configuration-space probability density $P(\mathbf{r}_1,\mathbf{r}_2,\ldots,\mathbf{r}_N,t)$ and the configuration-space current density $\mathbf{J}(\mathbf{r}_1,\mathbf{r}_2,\ldots,\mathbf{r}_N,t)$, are needed for a complete specification of the system. Nevertheless, any one of them is sufficient, as can be demonstrated following the argument of Dhara and Ghosh,[16] to determine the other, since the continuity equation is to be obeyed along with suitable boundary conditions on P and $\mathbf{J}$. The same conclusion about the uniqueness of the mapping $\rho(\mathbf{r},t)\rightarrow\mathbf{j}(\mathbf{r},t)$ in reduced space and hence $\rho(\mathbf{r},t)\rightarrow\mathbf{j}(\mathbf{r},t)\rightarrow v(\mathbf{r},t)$ remains valid as long as the external potential $v(\mathbf{r},t)$ is a scalar potential. The present work, however, shows that the presence of the vector potential alters the scene, and only the mapping $\mathbf{j}(\mathbf{r},t)\rightarrow\{\phi(\mathbf{r},t),\mathbf{A}(\mathbf{r},t)\}$ and $\mathbf{j}(\mathbf{r},t)\rightarrow\rho(\mathbf{r},t)$ is unique. Although it has not been proved conclusively that $\rho(\mathbf{r},t)\rightarrow\mathbf{j}(\mathbf{r},t)$ is not unique, perhaps the vector quantity $\mathbf{j}(\mathbf{r},t)$ is necessary to characterize the vector potential $\mathbf{A}(\mathbf{r},t)$ and the latter cannot be fixed by a scalar quantity $\rho(\mathbf{r},t)$ alone. In any case it is convenient to express the expectation values as functionals of both $\rho(\mathbf{r},t)$ and $\mathbf{j}(\mathbf{r},t)$.

Theorem 2. For the system considered here, the quantity

$$\tilde{Q}=\int dt\left\langle\psi\left|-i\hbar(\partial/\partial t)+T+U+V-e\sum_k\phi_k\right|\psi\right\rangle$$

is a functional of the density $\rho(\mathbf{r},t)$ and the current density $\mathbf{j}(\mathbf{r},t)$, where

$$T=(1/2m)\sum_k[\hat{\mathbf{p}}(\mathbf{r}_k)+(e/c)\mathbf{A}(\mathbf{r}_k,t)]^2$$

is the kinetic energy operator. For given $v(\mathbf{r})$, $\phi(\mathbf{r},t)$, and $\mathbf{A}(\mathbf{r},t)$ the stationary condition

$$\delta\tilde{Q}_{\{v\}}[\rho(\mathbf{r},t),\mathbf{j}(\mathbf{r},t)]=0$$

is obeyed at the correct solution point. Here $\{v\}$ stands for the set of potentials

$$\{v(\mathbf{r}),\phi(\mathbf{r},t),\,\mathbf{A}(\mathbf{r},t)\}$$

and when used as a subscript, it indicates that the potentials are held constant.

Proof. Since $v(\mathbf{r})$, $\phi(\mathbf{r},t)$, $\mathbf{A}(\mathbf{r},t)$, and $\psi(\mathbf{r}_1,\mathbf{r}_2,\ldots,\mathbf{r}_N,t)$ are already proved to be functionals of $\rho(\mathbf{r},t)$ and $\mathbf{j}(\mathbf{r},t)$, clearly $\tilde{Q}$ is a functional of them. After separating out the explicit potential-dependent terms, one can write

$$\begin{aligned}\tilde{Q}[\rho,\mathbf{j}]&=F[\rho,\mathbf{j}]+\int dt\int d\mathbf{r}\{\rho(\mathbf{r},t)[v(\mathbf{r})-e\phi]+(e/c)\mathbf{A}\cdot\mathbf{j}_p+(e/2c)\mathbf{A}\cdot\mathbf{j}_d\}\\&=F[\rho,\mathbf{j}]+\int dt\int d\mathbf{r}\{\rho(\mathbf{r},t)[v(\mathbf{r})-e\phi]+(e/c)\mathbf{A}\cdot\mathbf{j}(\mathbf{r},t)-(e^2/2mc^2)\mathbf{A}^2\rho(\mathbf{r},t)\}\ ,\end{aligned}\tag{22}$$

where $\mathbf{j}_p$ and $\mathbf{j}_d$ are the paramagnetic and the diamagnetic contributions to the current density $\mathbf{j}(\mathbf{r},t)$ given by

$$\mathbf{j}=\mathbf{j}_p+\mathbf{j}_d\ ,\tag{23a}$$

$$\mathbf{j}_p=-(i\hbar/2m)\left\langle\psi\left|\sum_k[\nabla_k\delta(\mathbf{r}-\mathbf{r}_k)+\delta(\mathbf{r}-\mathbf{r}_k)\nabla_k]\right|\psi\right\rangle\ ,\tag{23b}$$

$$\mathbf{j}_d=(e/mc)\left\langle\psi\left|\sum_k\mathbf{A}_k\delta(\mathbf{r}-\mathbf{r}_k)\right|\psi\right\rangle=(e/mc)\mathbf{A}(\mathbf{r},t)\rho(\mathbf{r},t)\ ,\tag{23c}$$

and $F[\rho,\mathbf{j}]$ is the universal functional

$$F[\rho,\mathbf{j}]=\int dt\langle\psi[\rho,\mathbf{j}]\,|\,T_0+U-i\hbar(\partial/\partial t)\,|\,\psi[\rho,\mathbf{j}]\rangle\ ,\tag{24}$$

with T_0 as the kinetic energy operator $-(\hbar^2/2m)\sum_k\nabla_k^2$. This functional F is defined for v-representable densities. The true density is of course v-representable and Kohn[18] has shown that the densities in the neighborhood also are v-representable. Therefore the functional is well defined for densities differing from the true one only by a small amount. If $(\rho_0,\mathbf{j}_0)$ are the true densities and ψ_0 the corresponding wave function, then

$$\tilde{Q}[\psi_0]=\tilde{Q}[\rho_0,\mathbf{j}_0]=\tilde{Q}_{\{v\}}[\rho_0,\mathbf{j}_0]\ ,\tag{25}$$

where the second equality is valid if the set of potentials

$\{v\}$ corresponds to $[\rho_0, \mathbf{j}_0]$, i.e., it yields $[\rho_0, \mathbf{j}_0]$ through the solution of the Schrödinger equation. Considering the densities $\{\rho_0+\delta\rho_0, \mathbf{j}_0+\delta\mathbf{j}_0\}$ in the neighborhood for which the wave function is $\{\psi_0+\delta\psi_0\}$, one can write

$$\tilde{Q}_{\{v\}}[\rho_0+\delta\rho_0, \mathbf{j}_0+\delta\mathbf{j}_0]-\tilde{Q}_{\{v\}}[\rho_0, \mathbf{j}_0] = \tilde{Q}_{\{v\}}[\psi_0+\delta\psi_0]-\tilde{Q}_{\{v\}}[\psi_0] \; . \tag{26}$$

The rhs is, however, zero (considering up to first order) due to the stationarity condition; therefore, the left-hand side (lhs) is also zero leading to the stationarity condition for the density functional $\tilde{Q}_{\{v\}}$, viz.,

$$\delta\tilde{Q}_{\{v\}}[\rho, \mathbf{j}]=0 \quad \text{at } \rho=\rho_0, \quad \mathbf{j}=\mathbf{j}_0 \; , \tag{27}$$

which can be exploited for the calculation of densities.

B. Practical schemes for the calculation of densities and the density functionals

Theorem 3. The exact $\rho(\mathbf{r},t)$ and $\mathbf{j}(\mathbf{r},t)$ are obtainable from the two hydrodynamical equations, viz., the continuity equation (14)

$$(\partial\rho/\partial t)+\nabla\cdot\mathbf{j}(\mathbf{r},t)=0$$

and the Euler-type equation

$$(\partial/\partial t)\mathbf{j}(\mathbf{r},t)=\mathbf{P}_{\{v\}}[\rho(\mathbf{r},t), \mathbf{j}(\mathbf{r},t)] \; , \tag{28}$$

where the vector $\mathbf{P}_{\{v\}}$ is a functional of $\rho(\mathbf{r},t)$ and $\mathbf{j}(\mathbf{r},t)$ for specified $\{v\}$.

Proof. The continuity equation is well known and the Euler equation of motion follows from Eq. (9), since ψ is considered as a functional of ρ and $\mathbf{j}$. One can simplify the expression further and write

$$\begin{aligned}\mathbf{P}_{\{v\}}[\rho(\mathbf{r},t), \mathbf{j}(\mathbf{r},t)] = &-(i/\hbar)\langle\psi(t)\,|\,[\hat{\mathbf{j}}_0, \hat{H}_0]\,|\,\psi(t)\rangle \\ &-(\rho/m)[\nabla v+e\mathbf{E}(r,t)] \\ &-(e/mc)(j\times\mathbf{B})\end{aligned} \tag{29}$$

where $\mathbf{E}$ and $\mathbf{B}$ are the electric and magnetic fields given by Eq. (20) and $\nabla\times\mathbf{A}$, respectively. The operators $\hat{\mathbf{j}}_0$ and $\hat{H}_0$ are obtained from Eqs. (5b) and (3), respectively, after dropping the terms involving ϕ and $\mathbf{A}$. The same equation (28) is also obtainable from the variational condition (27) subject to the continuity equation as a constraint. This relates $\mathbf{P}_{\{v\}}[\rho, \mathbf{j}]$ with the functional derivative of $F[\rho, \mathbf{j}]$.

Theorem 4. For any arbitrary (v-representable) current density $\mathbf{j}(\mathbf{r},t)$ and the corresponding electron density $\rho(\mathbf{r},t)$ [i.e., solution of the continuity equation], a Levy-type universal functional for time-dependent systems can be constructed as follows.

(i) Define

$$Q[\rho(\mathbf{r},t), \mathbf{j}(\mathbf{r},t)]=\int dt\langle\psi^s_{\rho,\mathbf{j}}\,|\,T_0+U-i\hbar(\partial/\partial t)\,|\,\psi^s_{\rho,\mathbf{j}}\rangle \; , \tag{30}$$

where $\psi^s_{\rho,\mathbf{j}}$ corresponds to the stationary point of the functional

$$\int dt\langle\psi_{\rho,\mathbf{j}}\,|\,T_0+U-i\hbar(\partial/\partial t)\,|\,\psi_{\rho,\mathbf{j}}\rangle$$

with respect to all $\psi_{\rho,\mathbf{j}}$'s that yield the particular density ρ and the current density $\mathbf{j}$.

(ii) The stationary solution of the functional

$$\begin{aligned}Q_{\{v\}}[\rho, \mathbf{j}]=Q[\rho, \mathbf{j}]&+\int dt\int d\mathbf{r}\,\rho(\mathbf{r},t)[v(\mathbf{r})-e\phi] \\ &+(e/c)\int dt\int d\mathbf{r}\;\mathbf{A}\cdot\mathbf{j} \\ &-(e^2/2mc^2)\int dt\int d\mathbf{r}\;\mathbf{A}^2\rho(\mathbf{r},t) \; ,\end{aligned} \tag{31}$$

with respect to the variations of ρ and $\mathbf{j}$ subject to the continuity equation as a constraint would yield the correct density and current density of a many-electron system for given $v(\mathbf{r})$, $\phi(\mathbf{r},t)$, and $\mathbf{A}(\mathbf{r},t)$.

Proof. Let C_j and D_ρ be the sets of N-representable current density and charge density, respectively. For each trial density $\rho\in D_\rho$ and current density $\mathbf{j}\in C_j$, one can construct the set $W^{\psi}_{\rho,\mathbf{j}}$ containing all antisymmetric N-particle wave functions $\{\psi_{\rho,\mathbf{j}}\}$ that yield the given $\rho(\mathbf{r},t)$ and $\mathbf{j}(\mathbf{r},t)$ (see Appendix A). The definition of $Q[\rho, \mathbf{j}]$ provides a prescription for selecting a particular member $\psi^s_{\rho,\mathbf{j}}$ from the set. For v-representable densities, the stationary property of the functional $Q[\rho, \mathbf{j}]$ of Eq. (30) follows from the Dirac-Frenkel TD variational principle. This also implies that $F[\rho, \mathbf{j}]$ of Eq. (24) is identical to $Q[\rho, \mathbf{j}]$ of Eq. (30).

For a given ρ and $\mathbf{j}$, the quantity $Q_{\{v\}}[\rho, \mathbf{j}]$ of Eq. (31) which can be rewritten as

$$Q_{\{v\}}=\int dt\left\langle\psi^s_{\rho,\mathrm{j}}\left|\mathrm{T}_0+\mathrm{U}-\mathrm{i}\hbar(\partial/\partial \mathrm{t})-\mathrm{e}\sum_{\mathrm{k}}\phi_{\mathrm{k}}-\mathrm{i}(\mathrm{e}\hbar/\mathrm{mc})\sum_{\mathrm{k}}\mathbf{A}_{\mathrm{k}}\cdot\nabla_{\mathrm{k}}+(\mathrm{e}^2/2\mathrm{mc}^2)\sum_{\mathrm{k}}\mathbf{A}_{\mathrm{k}}^2\right|\psi^s_{\rho,\mathrm{j}}\right\rangle \tag{32}$$

is clearly stationary with respect to variation in $\psi_{\rho,\mathrm{j}}$ since $Q[\rho, \mathbf{j}]$ is so. Thus, when $\{\rho, \mathbf{j}\}$ is again varied, the final stationary point corresponds to the stationary solution with respect to all $\psi^s_{\rho,\mathrm{j}}$'s for every $\{\rho, \mathbf{j}\}$. This would correspond to the same solution as would have been obtained by direct Dirac-Frenkel variation with respect to the wave function ψ, or the variation principle of Eq. (27).

Theorem 5. The exact single-particle density $\rho(\mathbf{r},t)$ and the current density $\mathbf{j}(\mathbf{r},t)$ of a many-electron system subjected to a particular $\phi(\mathbf{r},t)$ and $\mathbf{A}(\mathbf{r},t)$ can be obtained from

$$\rho(\mathbf{r},t)=\sum_k\psi_k^*(\mathbf{r},t)\psi_k(\mathbf{r},t) \tag{33}$$

and

$$\begin{aligned}\mathbf{j}(\mathbf{r},t)=-(i\hbar/2m)\sum_k&[\psi_k^*(\mathbf{r},t)\,\nabla\psi_k(\mathbf{r},t) \\ &-\psi_k(\mathbf{r},t)\,\nabla\psi_k^*(\mathbf{r},t)] \\ &+(e/mc)\rho(\mathbf{r},t)\,\mathbf{A}_{\mathrm{eff}}(\mathbf{r},t) \; ,\end{aligned} \tag{34}$$

where the $\{\psi_k\}$'s are the solutions of the single-particle TD Schrödinger-like equations

$$\{(1/2m)[-i\hbar\nabla+(e/c)\mathbf{A}_{\text{eff}}]^2+v_{\text{eff}}(\mathbf{r},t)\}\psi_k(\mathbf{r},t) = i\hbar(\partial\psi_k(\mathbf{r},t)/\partial t)\ . \tag{35}$$

Here, the effective scalar and vector potentials $v_{\text{eff}}(\mathbf{r},t)$ and $\mathbf{A}_{\text{eff}}(\mathbf{r},t)$ whose expressions will be derived below consist, respectively, of the external potentials $v(\mathbf{r})-e\phi(\mathbf{r},t)$ and $\mathbf{A}(\mathbf{r},t)$ supplemented by internal contributions arising from the density and the current-density distributions.

Proof. Define a functional $Q_0^s[\rho,\mathbf{j}]$ for a fictitious system of N noninteracting particles having the (v-representable) current density $\mathbf{j}(\mathbf{r},t)$ and the corresponding electron density $\rho(\mathbf{r},t)$ [i.e., the solution of the continuity equation], which are identical to those of the actual system of interest (where interaction is present), i.e.,

$$Q_0^s[\rho(\mathbf{r},t),\mathbf{j}(\mathbf{r},t)]=\int dt\langle\psi^s_{\rho,\mathbf{j}}\,|\,T_0-i\hbar(\partial/\partial t)\,|\,\psi^s_{\rho,\mathbf{j}}\rangle\ , \tag{36}$$

where $\psi^s_{\rho,\mathbf{j}}$ corresponds to the stationary point [see Eq. (30) with $U=0$]. This variation can be achieved by considering a single determinantal wave function and hence the stationary point of the functional

$$Q_0[\rho(\mathbf{r},t),\mathbf{j}(\mathbf{r},t)] = \sum_k\int dt\langle\psi_k\,|\,-(\hbar^2/2m)\nabla^2-i\hbar(\partial/\partial t)\,|\,\psi_k\rangle \tag{37}$$

with respect to the normalized single-particle orbitals $\{\psi_k\}$ subject to the constraints that the ψ_k's yield the given density $\rho(\mathbf{r},t)$ and the current density $\mathbf{j}(\mathbf{r},t)$ according to Eqs. (33) and

$$\mathbf{j}(\mathbf{r},t)=(1/2m)\sum_k\{\psi_k^*(\mathbf{r},t)\hat{\mathbf{p}}\psi_k(\mathbf{r},t) +[\hat{\mathbf{p}}\psi_k(\mathbf{r},t)]^*\psi_k(\mathbf{r},t)\}\ , \tag{38}$$

respectively, such that the continuity equation (14) is satisfied. Here, $\hat{\mathbf{p}}$ refers to the canonical momentum operator.

This constrained variation is equivalent to the Euler-Lagrange equation

$$\delta\left[Q_0[\rho,\mathbf{j}]-\int dt\int d\mathbf{r}\,\alpha(\mathbf{r},t)\left[(\partial/\partial t)\sum_k\psi_k^*(\mathbf{r},t)\psi_k(\mathbf{r},t)+\nabla\cdot(1/2m)\sum_k\{\psi_k^*(\mathbf{r},t)\hat{\mathbf{p}}\psi_k(\mathbf{r},t)+[\hat{\mathbf{p}}\psi_k(\mathbf{r},t)]^*\psi_k(\mathbf{r},t)\}\right]\right.$$
$$\left.-\int dt\int d\mathbf{r}\,\boldsymbol{\beta}(\mathbf{r},t)\cdot\left[(1/2m)\sum_k\{\psi_k^*(\mathbf{r},t)\hat{\mathbf{p}}\psi_k(\mathbf{r},t)+[\hat{\mathbf{p}}\psi_k(\mathbf{r},t)]^*\psi_k(\mathbf{r},t)\}-\mathbf{j}(\mathbf{r},t)\right]\right]=0\ , \tag{39}$$

where $\alpha(\mathbf{r},t)$ and $\boldsymbol{\beta}(\mathbf{r},t)$ are the Lagrange multipliers associated with the constraints of the continuity equation and the current density, respectively. Equation (39) leads to the set of single-particle equations,

$$[-(\hbar^2/2m)\nabla^2-i\hbar(\partial/\partial t)]\psi_k(\mathbf{r},t)+[(\partial/\partial t)\alpha(\mathbf{r},t)]\psi_k-(1/2m)[\boldsymbol{\beta}(\mathbf{r},t)-\nabla\alpha(\mathbf{r},t)]\cdot\hat{\mathbf{p}}\psi_k(\mathbf{r},t)$$
$$-(1/2m)\hat{\mathbf{p}}\cdot\{[\boldsymbol{\beta}(\mathbf{r},t)-\nabla\alpha(\mathbf{r},t)]\psi_k(\mathbf{r},t)\}=0\ . \tag{40}$$

Here, $\alpha(\mathbf{r},t)$ and $\boldsymbol{\beta}(\mathbf{r},t)$ are to be chosen so that the resultant orbitals $\{\psi_k(\mathbf{r},t)\}$ yield the desired $\rho(\mathbf{r},t)$ and $\mathbf{j}(\mathbf{r},t)$ satisfying the continuity equation. Premultiplying Eq. (40) by ψ_k^*, followed by summation over k and subtraction of the complex conjugate, one obtains

$$(\partial\rho/\partial t)=(i\hbar/2m)\nabla\cdot\sum_k(\psi_k^*\nabla\psi_k-\psi_k\nabla\psi_k^*)+(i/\hbar)(1/2m)(\boldsymbol{\beta}-\nabla\alpha)\cdot\sum_k[\psi_k^*\hat{\mathbf{p}}\psi_k-(\hat{\mathbf{p}}\psi_k)^*\psi_k]$$
$$+(i/\hbar)(1/2m)\sum_k(\psi_k^*\hat{\mathbf{p}}\cdot[(\boldsymbol{\beta}-\nabla\alpha)\psi_k]-\psi_k\{\hat{\mathbf{p}}\cdot[(\boldsymbol{\beta}-\nabla\alpha)\psi_k]\}^*)$$
$$=\nabla\cdot[(i\hbar/2m)\sum_k(\psi_k^*\nabla\psi_k-\psi_k\nabla\psi_k^*)]+(1/m)\nabla\cdot[(\boldsymbol{\beta}-\nabla\alpha)\rho(\mathbf{r},t)]\ , \tag{41}$$

where the second equality has been obtained by considering $\hat{\mathbf{p}}$ to be the sum of $-i\hbar\nabla$ and a real vector function. Equation (41) is the continuity equation and hence the quantity $\boldsymbol{\beta}-\nabla\alpha$ must represent an effective vector potential, i.e.,

$$(e/c)\mathbf{A}_{\text{eff}}(\mathbf{r},t)=-[\boldsymbol{\beta}(\mathbf{r},t)-\nabla\alpha(\mathbf{r},t)]\ , \tag{42a}$$

so that the canonical momentum operator is given by

$$\hat{\mathbf{p}}=-i\hbar\nabla+(e/c)\mathbf{A}_{\text{eff}}(\mathbf{r},t)\ , \tag{42b}$$

and the current density defined in Eq. (38) is given by Eq. (34).

Using Eq. (42), Eq. (40) simplifies to

$$[-(\hbar^2/2m)\nabla^2-i\hbar(\partial/\partial t)]\psi_k(\mathbf{r},t)+[(\partial/\partial t)\alpha(\mathbf{r},t)]\psi_k+(e/2mc)\mathbf{A}_{\text{eff}}(\mathbf{r},t)\cdot\hat{\mathbf{p}}\psi_k(\mathbf{r},t)$$
$$+(e/2mc)\hat{\mathbf{p}}\cdot[\mathbf{A}_{\text{eff}}(\mathbf{r},t)\psi_k(\mathbf{r},t)]=0\ , \tag{43a}$$

which can be rewritten as

$$\{(1/2m)[-i\hbar\nabla+(e/c)\mathbf{A}_{\text{eff}}]^2\psi_k(\mathbf{r},t)+[(\partial/\partial t)\alpha(\mathbf{r},t)]\psi_k(\mathbf{r},t)+(e^2/2mc^2)\mathbf{A}^2_{\text{eff}}(\mathbf{r},t)\}\psi_k(\mathbf{r},t)=i\hbar[\partial\psi_k(\mathbf{r},t)/\partial t]\ . \tag{43b}$$

Now, using Eqs. (37), (38), (40), and (42a), the functional $Q_0^s[\rho,\mathbf{j}]$ can be expressed as

$$Q_0^s[\rho,\mathbf{j}]=-\int dt\int d\mathbf{r}[(\partial/\partial t)\alpha(\mathbf{r},t)]\rho(\mathbf{r},t)-(e/c)\int dt\int d\mathbf{r}\ \mathbf{A}_{\text{eff}}(\mathbf{r},t)\cdot\mathbf{j}(\mathbf{r},t)\ , \tag{44}$$

and therefore the functional $Q_{\{v\}}[\rho,\mathbf{j}]$ of Eq. (31) can be rewritten as

$$\begin{aligned}Q_{\{v\}}[\rho,\mathbf{j}]=&-\int dt\int d\mathbf{r}\,\rho(\mathbf{r},t)[(\partial/\partial t)\alpha(\mathbf{r},t)]-(e/c)\int dt\int d\mathbf{r}\ \mathbf{A}_{\text{eff}}(\mathbf{r},t)\cdot\mathbf{j}(\mathbf{r},t)+U_{\text{int}}[\rho,\mathbf{j}]\\&+E_{\text{xc}}[\rho,\mathbf{j}]+\int dt\int d\mathbf{r}\,\rho(\mathbf{r},t)[v(\mathbf{r})-e\phi]+(e/c)\int dt\int d\mathbf{r}\ \mathbf{A}\cdot\mathbf{j}(\mathbf{r},t)-(e^2/2mc^2)\int dt\int d\mathbf{r}\ \mathbf{A}^2\rho(\mathbf{r},t)\ ,\end{aligned} \tag{45}$$

where the direct-interaction energy $U_{\text{int}}[\rho,\mathbf{j}]$ and the exchange-correlation energy $E_{\text{xc}}[\rho,\mathbf{j}]$ together account for the difference between $Q[\rho,\mathbf{j}]$ and $Q_0^s[\rho,\mathbf{j}]$.

The stationary solution $\delta Q_{\{v\}}[\rho,\mathbf{j}]=0$ (see Theorem 2) for variations in ρ and $\mathbf{j}$, respectively, lead to the equations

$$(e/c)\mathbf{A}_{\text{eff}}(\mathbf{r},t)-(e/c)\mathbf{A}(\mathbf{r},t)-(\delta U_{\text{int}}[\rho,\mathbf{j}]/\delta\mathbf{j})-(\delta E_{\text{xc}}[\rho,\mathbf{j}]/\delta\mathbf{j})=0 \tag{46a}$$

and

$$-(\partial/\partial t)\alpha(\mathbf{r},t)+(\delta U_{\text{int}}[\rho,\mathbf{j}]/\delta\rho)+(\delta E_{\text{xc}}[\rho,\mathbf{j}]/\delta\rho)+[v(\mathbf{r})-e\phi(\mathbf{r},t)]-(e^2/2mc^2)A^2=0\ . \tag{46b}$$

The variations of α and $\mathbf{A}_{\text{eff}}$ in Eq. (45) do not contribute to Eqs. (46), as can be shown by using Eq. (43) and the stationarity of $\{\psi_k\}$ at the end points with respect to time. Substituting the values of $(\partial/\partial t)\alpha(\mathbf{r},t)$ from Eq. (46b) into Eq. (43b), one obtains Eq. (35) where the effective vector potential $\mathbf{A}_{\text{eff}}(\mathbf{r},t)$ and the effective scalar potential $v_{\text{eff}}(\mathbf{r},t)$ are given by

$$\mathbf{A}_{\text{eff}}(\mathbf{r},t)=\mathbf{A}(\mathbf{r},t)+(c/e)(\delta U_{\text{int}}/\delta\mathbf{j})+(c/e)(\delta E_{\text{xc}}/\delta\mathbf{j}) \tag{47}$$

and

$$v_{\text{eff}}(\mathbf{r},t)=v(\mathbf{r})-e\phi(\mathbf{r},t)+(\delta U_{\text{int}}/\delta\rho)+(\delta E_{\text{xc}}/\delta\rho)+(e^2/2mc^2)(A^2_{\text{eff}}-A^2)\ , \tag{48}$$

respectively. The classical Coulomb energy U_{Coul} corresponding to the term U_{int} is given by

$$U_{\text{Coul}}[\rho]=\tfrac{1}{2}e^2\int\int d\mathbf{r}\,d\mathbf{r}'\rho(\mathbf{r},t)\rho(\mathbf{r}',t)/|\mathbf{r}-\mathbf{r}'|\ , \tag{49}$$

and therefore the corresponding potential is

$$\delta U_{\text{int}}/\delta\rho=\delta U_{\text{Coul}}/\delta\rho=e^2\int d\mathbf{r}'\rho(\mathbf{r}',t)/|\mathbf{r}-\mathbf{r}'|\ . \tag{50}$$

The analogous contribution in the vector potential, i.e., the term $(\delta U_{\text{int}}/\delta\mathbf{j})$ is usually ignored. However, if one considers the current-current interaction, the resultant potential is given by (see, e.g., Refs. 19–21)

$$\delta U_{\text{int}}/\delta\mathbf{j}=\int d\mathbf{r}'\mathbf{j}(\mathbf{r}',t)/|\mathbf{r}-\mathbf{r}'|\ . \tag{51}$$

Equation (35) is to be solved for $\rho(\mathbf{r},t)$ and $\mathbf{j}(\mathbf{r},t)$ self-consistently with the help of Eqs. (47)–(51), (33), and (34). The picture that emerges is that of a system of noninteracting particles moving in the effective scalar and vector potentials $v_{\text{eff}}(\mathbf{r},t)$ and $\mathbf{A}_{\text{eff}}(\mathbf{r},t)$, respectively. The calculated densities are, however, identical to those of the actual system of interest. For zero vector potential, the self-consistent equations become identical to the conventional time-dependent Kohn-Sham equations[8,9] for scalar potential alone.

Theorems 3–5 thus provide practical schemes for the calculation of the charge and current densities. While the hydrodynamical equations (14) and (28) can be solved for the two densities directly, for actual calculation, an explicit form of the first term on the rhs of Eq. (29) in terms of $\rho(\mathbf{r},t)$ and $\mathbf{j}(\mathbf{r},t)$ is to be developed. The Thomas-Fermi method and its variants would provide guidelines in this direction. The prescription of Theorem 4 uses wave functions constructed from densities as the intermediate quantities, and as a result can yield the wave function also at the solution point.

The scheme of density calculation within the orbital description through the solution of single-particle equations (35) with the effective potentials defined by Eqs. (47)–(51) and the densities calculated using Eqs. (33) and (34) is a generalization of the conventional Kohn-Sham procedure to include TD systems involving magnetic fields. Although in deriving these equations, Coulomb gauge has been implied, fixing a gauge does not alter the physical situation, and all physical properties should remain unaltered under gauge transformation. The present formulation does satisfy the important property of gauge invariance which we prove in Appendix B.

III. CONCLUDING REMARKS

The two main objectives of this paper have been to establish a Hohenberg-Kohn-like theorem demonstrating the uniqueness of the density-to-potential mapping for many-electron systems characterized by scalar as well as vector potentials with arbitrary time dependence, and to provide thereby a theoretical framework for the direct calculation of the charge and current densities. The present generalization would enable one to discuss an important TD phenomenon, viz., the interaction of radiation with matter using a density-based approach. This broadens the scope of DFT and is thus significant in the context of recent attempts to explore the possibility of an alternative quantum mechanics in terms of density quantities rather than the wave function.

We have shown that it is the current density which determines both the scalar and vector potentials and hence plays the major role in cases involving magnetic fields.[22] The electron density is also determined by the current density through the continuity equation and is by itself sufficient only for problems involving no magnetic field and several other simple situations (see Theorem 1). The hydrodynamic equations proposed[23] earlier from phenomenological considerations for the study of surface properties and other problems now find a more rigorous justification in Theorem 3.

Although the hydrodynamical equations can be directly solved for the densities, the Kohn-Sham-type scheme provided by Theorem 5 would be more promising. With proper choice of exchange-correlation energy density functionals, accurate predictions of $\rho(\mathbf{r},t)$ and $\mathbf{j}(\mathbf{r},t)$ are possible through this route. The same framework can also be employed for developing a theory of magnetic properties[20] of many-electron systems. This would supplement the earlier studies on frequency-dependent electric polarizabilities[24] of atoms and molecules. A variety of dynamic phenomena can in fact be explored by using the time-dependent density-functional theory.

ACKNOWLEDGMENTS

It is a pleasure to thank H. K. Sadhukhan and Dr. S. V. Lawande for their kind interest and encouragement.

APPENDIX A: CONSTRUCTION OF WAVE FUNCTIONS $\{\psi_{\rho,\mathbf{j}}\}$ CORRESPONDING TO GIVEN DENSITY $\rho(\mathbf{r},t)$ AND CURRENT DENSITY $\mathbf{j}(\mathbf{r},t)$

For a particular wave function ψ, the electron density $\rho(\mathbf{r},t)$ as well as the paramagnetic current density $\mathbf{j}_p(\mathbf{r},t)$ are easily obtained through Eqs. (4a) and (23b), respectively. However, due to the dependence of the diamagnetic current density $\mathbf{j}_d(\mathbf{r},t)$ on the vector potential [see Eq. (23c)], one requires the knowledge of this additional potential for obtaining the net current density $\mathbf{j}(\mathbf{r},t)$ using Eq. (23a). In this Appendix, we address the inverse problem, i.e., the construction of a wave function ψ that yields a given (v-representable) $\rho(\mathbf{r},t)$ and $\mathbf{j}(\mathbf{r},t)$.

Because of v-representability, the chosen $\rho(r,t)$ and $\mathbf{j}(\mathbf{r},t)$ have associated with them (see Theorem 1) a unique vector potential $\mathbf{A}[\mathbf{j}]$. In attempting to obtain the wave functions $\psi_{\rho,\mathbf{j}}$, it is this vector potential $\mathbf{A}[\mathbf{j}]$ which is to be employed in the diamagnetic term in defining $\mathbf{j}(\mathbf{r},t)$ through Eq. (23). For v-representable densities, it is obvious that the set $W^{\psi}_{\rho,\mathbf{j}}$ containing such wave functions is not empty. It would, however, be of interest to discuss an explicit construction of such wave functions from given ρ and $\mathbf{j}$ satisfying the N-representability conditions

$$\rho \geq 0 \; ,$$

$$\int d\mathbf{r}\,\rho(\mathbf{r},t) = N \; ,$$

$$\int d\mathbf{r}\;\mathbf{j}_p(\mathbf{r},t)/\rho(\mathbf{r},t) = \text{finite} \; .$$

Such constructions are also of importance in executing a variational procedure. The simplest case arises when the wave function is represented by a single determinant constructed from a set of orthonormal orbitals[25,26] of equal electron density. We consider only the one-dimensional case for simplicity (the extension to three dimensions is straightforward) and define the quantities

$$q(x) = \int_a^x dx' \rho_1(x') \; ,$$

i.e., (A1)

$$\rho_1(x) = (dq/dx) \; ,$$

$$s(x) = \int_a^x dx' [\mathbf{j}_p(x')/\rho(x')] \; ,$$

i.e., (A2)

$$\mathbf{j}(x) = \rho(x)(ds/dx) + (e/mc)\rho(x) A[\mathbf{j}] \; ,$$

where ρ_1 $(=\rho/N)$ is the density normalized to unity and $a \leq x \leq b$. Also, as already stated, $\mathbf{A}[\mathbf{j}]$ is the vector potential uniquely determined by the current density $\mathbf{j}(\mathbf{r},t)$. Now the set of orthonormal orbitals $\{\psi_k\}$ can be constructed with

$$\psi_k(x) = \rho_1^{1/2}(x) \exp\{ i 2\pi [kq - (ms/2\pi\hbar) - (M/N)q] \} \; . \tag{A3}$$

Here, the orthonormality $\langle \psi_k \mid \psi_{k'} \rangle = \delta_{kk'}$ is maintained provided k and k' differ by integers, i.e., $k=0, \pm 1, \pm 2$, etc. or $k = \pm\frac{1}{2}, \pm\frac{3}{2}$, etc. An optimum selection for the k values depending on the number of electrons so as to correspond to a minimum of kinetic energy has been discussed elsewhere.[25] The integer M which appears in all orbitals is, however, to be selected based on the k values of all the occupied orbitals so that one obtains the correct current density. The contribution to the paramagnetic current density from the kth orbital is given by

$$\begin{aligned} \mathbf{j}_k(x) &= -(\hbar/m)\rho_1(x)\nabla\{2\pi[kq - (ms/2\pi\hbar) - (M/N)q]\} \\ &= -(\hbar/m)\rho_1^2(x) 2\pi(k - M/N) + \mathbf{j}_p/N \; . \end{aligned} \tag{A4}$$

Thus, for the choice $\sum_k k = M$, these orbitals yield the correct current density,

$$\mathbf{j} = \sum_k \mathbf{j}_k + (e/mc)\rho\,\mathbf{A}[\mathbf{j}] \; . \tag{A5}$$

It can be shown[25] that for an even number of electrons the minimum kinetic energy corresponds to using half integer or integer values of k, depending on whether N is a multiple of 4 or not. In such cases, the value of M can be chosen as zero since the k-dependent terms in the phases do not contribute to the net current density. For an odd number of electrons, the value of k for the highest occupied orbital can be assigned to M. The present construction thus provides a set of orthonormal orbitals (and hence a corresponding determinantal wave function) for a given ρ and $\mathbf{j}$.

APPENDIX B: GAUGE INVARIANCE OF THE TIME-DEPENDENT KOHN-SHAM-LIKE SINGLE-PARTICLE EQUATIONS INVOLVING VECTOR POTENTIALS

The TD Kohn-Sham-like single-particle equations [Eq. (35)] are used to obtain self-consistent solutions for $\rho(\mathbf{r},t)$ and $\mathbf{j}(\mathbf{r},t)$ using Eqs. (33) and (34) with the effective scalar and vector potentials $v_{\text{eff}}(\mathbf{r},t)$ and $\mathbf{A}_{\text{eff}}(\mathbf{r},t)$ given, respectively, by Eqs. (48) and (47). Besides having an explicit dependence on the external scalar and vector potentials $\phi(\mathbf{r},t)$ and $\mathbf{A}(\mathbf{r},t)$, these effective potentials have contributions from internal potentials arising from the charge- and current-density distributions as well. The formalism has been developed using the Coulomb gauge ($\nabla\cdot\mathbf{A}=0$) for simplicity. The quantities of significance are, however, the applied electric and magnetic fields $\mathbf{E}(\mathbf{r},t)$ and $\mathbf{B}(\mathbf{r},t)$ defined through Eq. (20) and ($\nabla\times\mathbf{A}$), respectively. While the potentials obtained using the Coulomb gauge correspond to these fields, one can have other potentials as well for the same fields using the gauge transformations of the potentials, viz.,

$$\mathbf{A}\rightarrow\mathbf{A}'=\mathbf{A}+\nabla\lambda(\mathbf{r},t)\ , \tag{B1a}$$

$$\phi\rightarrow\phi'=\phi-(1/c)(\partial/\partial t)\lambda(\mathbf{r},t)\ , \tag{B1b}$$

where $\lambda(\mathbf{r},t)$ is an arbitrary function. Our aim, in this Appendix, is to show that the present formulation is properly gauge invariant with respect to these gauge transformations. It is clear that the density $\rho(\mathbf{r},t)$ and the current density $\mathbf{j}(\mathbf{r},t)$ which are physical observables are invariant under these transformations. This result follows from the transformation of the full Schrödinger wave function under change in gauge, viz.,

$$\psi\rightarrow\psi'=\psi\exp[-(ie/\hbar c)\sum_k\lambda(\mathbf{r}_k,t)] \tag{B2}$$

and the definitions of $\rho(\mathbf{r},t)$ and $\mathbf{j}(\mathbf{r},t)$ through Eqs. (4) and (5), respectively. The paramagnetic and the diamagnetic counterparts of the current density, i.e., $\mathbf{j}_p(\mathbf{r},t)$ and $\mathbf{j}_d(\mathbf{r},t)$ individually, however, are not gauge-invariant quantities and depend on $\lambda(\mathbf{r},t)$, viz.,

$$\mathbf{j}_p\rightarrow\mathbf{j}_p'-(e/mc)\rho(\mathbf{r},t)\nabla\lambda(\mathbf{r},t)\ , \tag{B3}$$

$$\mathbf{j}_d\rightarrow\mathbf{j}_d'=\mathbf{j}_d+(e/mc)\rho(\mathbf{r},t)\nabla\lambda(\mathbf{r},t)\ . \tag{B4}$$

For considering the effect of the gauge transformations (B1) on Eq. (35), let us first transform all the single-particle orbitals $\{\psi_k\}$ through a phase factor, i.e.,

$$\psi_k\rightarrow\psi_k'=\psi_k\exp[-(ie/\hbar c)\lambda(\mathbf{r},t)]\ . \tag{B5}$$

Applying this transformation to Eq. (34), it is clear that the effective vector potential $\mathbf{A}_{\text{eff}}$ has to transform as

$$\mathbf{A}_{\text{eff}}\rightarrow\mathbf{A}_{\text{eff}}'=\mathbf{A}_{\text{eff}}+\nabla\lambda(\mathbf{r},t) \tag{B6}$$

in order to maintain the gauge invariance of the current density $\mathbf{j}(\mathbf{r},t)$. Equation (B6) also implies that under gauge transformation, the last term of Eq. (48) transforms as

$$\begin{aligned}(e^2/2mc^2)(A_{\text{eff}}'^2-A'^2)=&(e^2/2mc^2)(A_{\text{eff}}^2-A^2)\\&+(e^2/mc^2)(\mathbf{A}_{\text{eff}}-\mathbf{A})\cdot\nabla\lambda\ .\end{aligned} \tag{B7}$$

Now, using the transformation (B2) to $\psi_{\rho,\mathbf{j}}$ of Eq. (30), the functional $Q[\rho,\mathbf{j}]$ is transformed to $Q'[\rho,\mathbf{j}]$, i.e.,

$$\begin{aligned}Q\rightarrow Q'=Q&-(e/c)\int dt\int d\mathbf{r}\,\nabla\lambda\cdot[\mathbf{j}-(e/mc)\mathbf{A}\rho]\\&+(e^2/2mc^2)\int dt\int d\mathbf{r}\,\rho\,\nabla\lambda\cdot\nabla\lambda\\&-(e/c)\int dt\int d\mathbf{r}\,\rho(\partial\lambda/\partial t)\ .\end{aligned} \tag{B8}$$

Analogously, using Eq. (B5), Q_0^s corresponding to Eq. (37) leads to

$$\begin{aligned}Q_0^s\rightarrow Q_0^{s\prime}=Q_0^s&-(e/c)\int dt\int d\mathbf{r}\,\nabla\lambda\cdot[\mathbf{j}-(e/mc)\mathbf{A}_{\text{eff}}\rho]\\&+(e^2/2mc^2)\int dt\int d\mathbf{r}\,\rho\nabla\lambda\cdot\nabla\lambda\\&-(e/c)\int dt\int d\mathbf{r}\,\rho(\partial\lambda/\partial t)\ .\end{aligned} \tag{B9}$$

Since $(Q-Q_0^s)=(U_{\text{int}}+E_{\text{xc}})$, one has the result

$$(U_{\text{int}}+E_{\text{xc}})'=(U_{\text{int}}+E_{\text{xc}})-(e^2/mc^2)\int dt\int d\mathbf{r}\,\rho(\mathbf{r},t)\nabla\lambda(\mathbf{r},t)\cdot(\mathbf{A}_{\text{eff}}-\mathbf{A})\ . \tag{B10}$$

The direct-interaction energy U_{int} comprises the classical Coulomb energy U_{Coul} of Eq. (49) and a contribution from the current-current interaction corresponding to Eq. (51). It is therefore a functional of ρ and $\mathbf{j}$ only and hence is gauge invariant. Hence Eq. (B10) reduces to

$$(E_{\text{xc}}'-E_{\text{xc}})=-(e^2/mc^2)\int dt\int d\mathbf{r}\,\rho(\mathbf{r},t)\nabla\lambda(\mathbf{r},t)\cdot(\mathbf{A}_{\text{eff}}-\mathbf{A})\ . \tag{B11}$$

Therefore one has the relation

$$\begin{aligned}&(\delta E_{\text{xc}}/\delta\rho)_j'-(\delta E_{\text{xc}}/\delta\rho)_j\\&\qquad=-(e^2/mc^2)\nabla\lambda(\mathbf{r},t)\cdot(\mathbf{A}_{\text{eff}}-\mathbf{A})\ ,\end{aligned} \tag{B12}$$

where $\mathbf{A}_{\text{eff}}$ has been treated as a functional of $\mathbf{j}(\mathbf{r},t)$ alone, since the continuity equation is implied in the definition of $\mathbf{A}_{\text{eff}}$.

Equations (B7) and (B12) imply that the transformed effective scalar potential of Eq. (48) becomes

$$\begin{aligned}v_{\text{eff}}'(\mathbf{r},t)=&v(\mathbf{r})-e\phi'(\mathbf{r},t)+(\delta U_{\text{int}}/\delta\rho)\\&+(\delta E_{\text{xc}}/\delta\rho)+(e^2/2mc^2)(A_{\text{eff}}^2-A^2)\\=&v_{\text{eff}}(\mathbf{r},t)+(e/c)(\partial\lambda/\partial t)\ ,\end{aligned} \tag{B13}$$

where the second equality is obtained using Eq. (B1).

The transformations of the effective scalar and vector potentials given by Eqs. (B13) and (B6), respectively, and the transformation of the single-particle orbitals $\{\psi_k\}$ given by Eq. (B5) [due to the gauge transformations of Eqs. (B1)] imply clearly that Eq. (35) is gauge invariant.

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[22] While our paper was being considered for publication, there appeared a paper in November, 1987 by G. Vignale and M. Rasolt, Phys. Rev. Lett. **59**, 2360 (1987), on density-functional theory in strong magnetic fields. The work of Vignale and Rasolt (VR) is, however, restricted to the time-independent domain alone. Moreover, apart from the electron density $\rho(\mathbf{r})$, the other basic variable used in the VR formalism is the paramagnetic current density $\mathbf{j}_p(\mathbf{r})$, which itself is not gauge invariant. Our independent work, on the other hand, deals with the more generalized time-dependent potentials and also employs the quantities $\rho(\mathbf{r},t)$ and $\mathbf{j}(\mathbf{r},t)$, both of which are gauge-invariant objects. Thus our formalism is physically more appealing and also has a scope of wider applicability. The self-consistent single-particle equations in both cases are, however, gauge invariant, but this appears to be more transparent in our formalism.

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